INFLIGHT RESISTANCE MEASUREMENTS ON HIGH-Tc SUPERCONDUCTING THIN FILMS EXPOSED TO ORBITAL ATOMIC OXYGEN ON CONCAP-II (STS-46)

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ABSTRACT

In 1992, UAH conducted a unique experiment on STS-46 in which $YBa_2Cu_3O_7$ (commonly known as "1-2-3" superconductor) high-T_c superconducting thin film samples prepared at three different laboratories were exposed to 5 eV atomic oxygen in low Earth orbit on the ambient and 320°C hot plate during the first flight of the CONCAP-II [Complex Autonomous Payload] experiment carrier.

The resistance of the thin films was measured in flight during the atomic oxygen exposure and heating cycle. Superconducting properties were measured in the laboratory

before and after the flight by the individual experimenters. Films with good superconducting properties, and which were exposed to the oxygen atom flux, survived the flight including those heated to 320° C (600 K) with properties essentially unchanged, while other samples which were heated but not exposed to oxygen were degraded. The properties of other flight controls held at ambient temperature appear unchanged and indistinguishable from those of ground controls, whether exposed to oxygen or not.

INTRODUCTION

The effect of low Earth environment (LEO) on spacecraft has been the subject of several flight experiments over the past decade. Among these, the long duration exposure facility (LDEF) which remained in space for nearly 6 years has provided a wealth of data [1] that is invaluable from the standpoint of manufacture of long-lived spacecraft such as Space Station Freedom. Other flight experiments, such as STS-8 and 41-G [2] which studied atomic oxygen effects, provided data which was passive and there remain many unanswered questions as to the *in-situ* effects of atomic oxygen in the actual orbital environment on spacecrafts operating at altitudes between 200 and 900 km in LEO. The sticking coefficient of atomic oxygen on many materials such as silver and osmium is close to one [3]. It is important to understand the changes in the surface chemistry of many materials due to atomic oxygen and other induced environmental effects in low Earth orbit which is essential for the design of future spacecraft and many communication satellites.

A few years ago, a ceramic high temperature superconductor (HTSC), $YBa_2Cu_3O_7$, was discovered at the University of Alabama in Huntsville by M.K. Wu and J.R. Ashburn [4]. This work was partially funded by the UAH-NASA Consortium for Materials Development in Space (CMDS). Since that time, hundreds of millions of dollars have been spent on research worldwide into these ceramic systems, and although similar materials have been discovered with even higher critical temperatures than the 90 K of the UAH material, none has yet matched its combination of high-T_c and current-carrying capacity. In spite of many advances made in preparation of stable high quality devices from $YBa_2Cu_3O_7$, particularly those in thin film form, many materials processing problems remain with this material which continue to prevent its widespread use. Among the problems are those associated with very high temperature annealing required to obtain the superconducting phase with the proper quality, and the ease with which the material can lose oxygen [5,6].

Quite independently from the HTSC work, another UAH group had been studying the effect of fast atomic oxygen upon the surfaces of materials exposed in low Earth orbit. This work began in 1975 with the design of an experiment for NASA's Long Duration Exposure Facility (LDEF) and continued with flights on other carriers such as STS-8 in 1984. Under the conditions of bombardment by 5 eV atomic oxygen atoms new chemistry occurs, opening up the possibility of novel processing techniques using fast neutral beams. One of the longevity materials studied extensively on LDEF and also on the CMDS carrier CONCAP-II (STS-46) is copper and its oxides. We have shown that a pure copper surface is oxidized to a depth of 500 Å at room temperature when subjected to 5 eV atomic oxygen [7]. The stable oxide thickness at the same temperature in air is about 40 Å. Further work on CONCAP-II has shown that this oxide film may grow much thicker at 100-200°C.

Since both the conductivity and superconductivity of the cuprate class of HTSC's has been unequivocally shown to be associated with the copper oxide planes in the crystal lattice [8], a specific project was developed to probe the possibilities of low temperature

processing of these cuprate materials with fast atomic oxygen. The CMDS experiment carrier CONCAP-II was designed and built to accommodate these experiments (among others). The experiments were performed successfully in early August 1992, and some results are discussed below. High quality thin film HTSC devices were prepared by several leading U.S. laboratories including General Electric, Lockheed, LANL, and SUNY Buffalo.

The CONCAP-II-01 payload flew on space shuttle Atlantis, mission STS-46, on July 31, 1992, and was sponsored by the Consortium for Materials Development in Space (CMDS), at the University of Alabama in Huntsville (UAH). The CMDS is one of the Centers for the Commercial Development in Space funded jointly by NASA and private sector companies interested in promoting the commercialization of space. The UAH served as the integrator of CONCAP-II.

The payload contained an electronic controller and data system which monitored and recorded electrical resistance of 24 material samples of diverse composition. The system also controlled a hot plate at 320°C, the highest temperature at which material studies of this kind have been conducted in space.

OBJECTIVES

The objectives of the experiment were:
* To assess the survivability of thin film HTSC devices in the space environment at both ambient (300K) and elevated (600K) temperatures.
* To determine if fast oxygen atom bombardment may prevent loss of lattice oxygen from the HTSC's essential to performance.
* To determine if lost lattice oxygen may be replaced at relatively low temperatures by the fast O atom beam.

The first two objectives were successfully realized on STS-46. The third objective could not be achieved because of constraints on experimental complexity and shuttle operations. This objective will be sought during a re-flight of CONCAP-II in early 1994.

INSTRUMENTATION

a: CONCAP-II.01 Hardware

CONCAP-II utilized a Get Away Special (GAS) carrier system fitted into the space shuttle payload bay. The 5-cubic-foot GAS canister had a hermetically-sealed motorized door assembly (MDA) which protected samples and sensitive surfaces during all ground and flight operations, other than the exposure period itself (see figure 1). The HTSC and longevity samples contained in sample holders were mounted on the top surface "Experiment Insert Plate" and figure 2 shows the distribution of sample holders experiment and the location of electrical connectors. The experiment support equipment, including support electronics and a power supply, were mounted inside the sealed cannister.

CONCAP-II had an electronic experiment controller and a data system to record resistance measurements of up to 32 samples several times per minute during exposure, as well as a hot plate capable of maintaining samples at 320°C, the highest temperature at which materials studies of this kind have been conducted in space.

The support electronics provided for temperature control of the hot plate, multiplex sample-resistance measurements, and storage of all measured resistance, oxygen flux and temperature data. The power system included a Solid Rocket Booster (SRB) battery, solid state switch and DC/DC converter to supply the heater and monitor electronics. It supplied 1.4 kW-hrs of power at 28V. Also provided is a separate temperature recorder for all mission phases including transportation, launch and landing.

CONCAP's power supply and data acquisition/storage system are self-contained, requiring no shuttle interface, and are adaptable for other kinds of experiments as well. The 80C86 microprocessor-based data and control system is capable of sampling up to 32 analog channels and uses a 12-bit analog to digital converter. A block of data is sampled and stored every 10 seconds. There is an initial start up delay of 1 minute before data is taken to help prevent false starts. The time and experiment status are also stored in each data block. The experiment status contains information such as whether the shuttle is in the RAM-direction and whether the heater is presently on.

The experiment hardware is capable of being turned on and off up to 123 separate times and logging separate data segments for each power-on. The mission-elapsed timer is reset upon each power-on sequence. The memory can hold approximately 20.7 hours of data.

b: Processor Specifications

- Microprocessor-based (80C86) CPU running at 2.457 MHz
- Serial communications port Baud Rate: 300, 2400, or 38.4k
- Parallel port-   A total of three 8 bit ports:

  8 bit output   - 6 non-buffered outputs

  - 2 optically isolated outputs

  (heater control is one output)

  8 bit inputs -RAM direction is one input

  8 bit input/output- Undefined

- Timer   - Configured as a mission-elapsed timer. (Time since power on is available in hours, minutes, seconds)

- Memory-   I. Static ram - 4k bytes (stack/variable)

  II. Eprom   - 64 bytes (program memory)

  III. EEprom - upto 512k bytes (Data storage-non volatile)

- Analog channels   - 32 analog data channels

  (4-wire resistance measurements, current source)

  Four ranges: 0-200 ohms, 2.5mA

  0-4k ohms, 0.125mA

  0-10k ohms, 50 mA

  0-20k ohms, 25 mA

- Analog to Digital Converter   - 12 bit

c: Mission Description

CONCAP-II experiment was carried on mission STS-46 of space shuttle Atlantis in early August 1992. The shuttle was in a nominal 28.5° inclination orbit during the experiment exposure, and was flown at a relatively low altitude to maximize the O-atom exposure during the limited experiment time of 20 hours. The shuttle was oriented so that the normal to the cargo bay was within ±1° of the velocity vector. This ensured that most of the atmospheric O-atoms struck the experimental surfaces at close to normal incidence .

The exposure was made towards the end of the STS-46 mission, with the shuttle at 123 nautical miles (228 km) altitude. The atomic oxygen fluence was calculated using the MSIS-86 model of the atmosphere and a Johnson Space Center orbital mechanics program [9]. The experimental surfaces on CONCAP-II were protected from ambient contamination during all ground and orbital operations by a hermetically sealing lid (motorized door assembly) which was operated by the shuttle crew. The lid was opened after the shuttle had been maneuvered into the correct attitude and closed before leaving this attitude. During the time the lid was open, the average arriving flux of O-atoms was calculated to be 1.35×10^{15} cm^{-2}s^{-1}. At this flux, each surface atom on a sample is struck by a fast O-atom about once per second. The total exposure time for CONCAP was 20 hrs for an accumulated fluence of 1×10^{20} atoms cm^{-2}, with the 320° C hot plate energized for only about 10 hours. The following table gives the flight operations and the experiment elapsed-times.

Flight Operations	Experiment Elapsed Time
Orbiter in correct attitude Power to CONCAP controller MDA (lid) open at Mission-Elapsed Time 5 days: 22 hr: 42 min	0
Hot plate on	4 hr: 3 min
Temporary de-activation of hot plate	4 hr: 34 min
Reactivate hot plate	5 hr: 33 min
Hot plate off	15 hr: 16 min
CONCAP MDA closed, controller off	20 hr: 50 min

SAMPLE PREPARATION

The sample holders for the HTSC thin films shown in figure 3 were small, square integrated circuit mounts made of gold-plated Kovar supplied by Airpax, MD. Films were prepared at three different laboratories, General Electric, Schenectady (GE); Los Alamos National Laboratory (LANL); and SUNY, Buffalo. While prepared by different methods and deposited on several different substrates (MgO, $SrTiO_3$, $LaAlO_3$, YSZ and $NdGaO_3$), all were high-performance $YBa_2Cu_3O_7$ films with $T_c \sim 80 - 90K$ and $J_c > 1MA\ cm^{-2}$. All were thin, 0.14 to 0.6 μm, to maximize surface processing effects and were configured as bridges with the resistive element ~ 100 ohm (at room temperature) to match the measuring circuit performance. Details of the individual films are given in the results section below. GE films were prepared by co-evaporation, SUNY films by laser ablation, and LANL films by sputtering. No influence of preparation method on the flight measurements was observed. Figure 4 shows a representative HTSC device mounted in a flatpack.

UAH supplied each HTSC investigator with the appropriate number of flatpack device holders. The chips containing the thin film HTSC elements were installed by the individual co-investigators using either Aramco 569 or 571 high temperature adhesives. The adhesive layer was made as thin as possible to provide good heat conduction between chip and holder, and to avoid outgassing contamination. The flight measuring system needed only pins 1, 3, 7 and 10 as shown in figure 3 for the 4-point resistance measurement. Electrical connections within the mounts were made by conventional thermal acoustic bonding methods. External leads to the mounts were connected to the CONCAP measuring system. Mounting of the samples was done at Goddard Space Flight Center as late as possible before the flight and final changes were made at Kennedy Space Center prior to closing the motorized door assembly and final testing of the CONCAP-II controller and measuring system. The mask for holding the flatpacks mounted with HTSC films is shown in figure 5.

RESULTS

Two platinum resistance thermometers were used to monitor and control the heaters for the 320°C plate. Figure 6 shows the temperature profile of an RTD on the hot plate during the 20 hr CONCAP-II experiment. The heater system performed well in maintaining the temperature of the plate within the control band of ± 20° C. Two additional features may be noted. During periods when the plate was near ambient (0 - 50°C), the effect of solar heating may be seen, modulated by the orbital period. Since the platinum detector elements are inside the 0.25 inch thick aluminum heater plate, this effect (of the order of 10°C peak-to-peak) is much less than the solar heating effects on the HTSC elements, which also acted as thermometers. Another feature in the figure, the large spike occurring just before the sustained high temperature period, was caused by the crew shutting off the power to the CONCAP-II heaters since it was reported that the MDA (lid) had not opened. After about one hour, lid opening was verified and heater power reapplied.

Notes on General Electric HTSC thin films

Four samples were supplied, all from the same run and were 0.6 μm $YBa_2Cu_3O_7$ on $LaAlO_3$ substrates. They were post-annealed in O_2 at 30Pa and 1025K. Typical low

temperature properties were $T_c=90 \pm 1$ K, $J_c \sim 1\text{-}2$ MA cm^{-2} at 77K. On each substrate there were several bridges, but only one was monitored during flight. The four samples were mounted in two pairs: one pair at ambient temperature (~ 300K) during the exposure and one pair at 590 K. One sample of each pair was shielded from the atomic oxygen flux and would have been at the ambient pressure of $\sim 10^{-6}$ torr in the shuttle cargo bay. The laboratory control samples were stored at room temperature in flowing oxygen.

Figures 7 and 8 show the normalized resistance versus mission-elapsed time (MET) plot of GE 1 , and GE 3 (exposed) and GE 4 (covered) samples on the 320° C hot plate and the ambient plates, respectively. The effect of solar heating on the samples is evident from the periodic peaks which occur every 90 mins of shuttle cycle. Not much change in resistance is observed with the samples on the ambient plate. The sample on the hot plate showed the highest change in resistance when the heat was turned on. This can be attributed to the better quality of the film since it is known that the steeper the slope, the better the sample, which, in turn, suggests better critical current density. As can be seen from this plot, there is a slight change in resistance after ~MET 400 (mins). This may be attributed to contact annealing. Post-flight T_c was the same as the corresponding laboratory control sample. However the GE 2 sample on the hot plate, which was covered, was totally degraded due to loss of lattice oxygen. The following table shows the T_c values of the samples before and after the flight.

Sample	T_c (Before)	T_c (After)
GE 1 (Hot Plate, Exposed)	91 ± 1 K	91 ± 1 K
GE 2 (Hot Plate, Covered)	90 ± 1 K	Non-superconding
GE 3 (Ambient plate, Exposed)	90 ± 1 K	91 ±1 K
GE 4 (Ambient Plate, Covered)	91 ± 1 K	91 ± 1 K
GE 5 (Laboratory Control)	91 ± 1 K	91 ± 1 K

Notes on SUNY-prepared HTSC thin films

SUNY supplied 6 samples- four of which were for R-measurement (on ambient and hot plates) and the remaining two for exposure on the ambient plate. All films were prepared by laser ablation and were the thinnest of all those flown: 0.14 to 0.16 μm. For all films flown, except sample SUNY # 6, the values of J_c and T_c obtained before the flight, and after the flight several months later, were unchanged or degraded no more than those for the ground control. SUNY #6 was mounted using a special high temperature tape to the flatpack. The flight resistance data is shown in figure 9. The resistance can be seen to steadily increase after the control temperature of 320°C had been reached. Post-flight testing showed T_c to have dropped from 84.7K to 54.5K. Since this did not occur to sample SUNY # 3, (figure 10) which was attached with high temperature epoxy, or to any other film exposed to oxygen atoms during the flight, it is suspected that a component of the tape adhesive migrated into the HTSC film at 320°C and degraded its properties. While figure 9 (SUNY # 3) shows a decrease in resistance during the high temperature phase, this may be attributed to Contact annealing. The before and after test data is given below.

BEFORE AND AFTER FLIGHT TESTING OF SUNY HTSC SAMPLES

Sample	Substrate	Testing Condition	J_c (MA cm^{-2}) (before)	(after)	T_c(K) (before)	(after)
SUNY 1	YSZ	Low temp. active	1.6	1.4	82.9	82.0
SUNY 2	SrTiO$_3$	Ambient	1.07	2.21		82.9
SUNY 3	LaAlO$_3$	High temp. active	-	0.84		80.32
SUNY 4	LaAlO$_3$	Ambient	1.13	1.1	82.0	82.22
SUNY 5	YSZ	Low temp. active	1.6	0.0004	80.2	82.9
SUNY 6	SrTiO$_3$	High temp. active	1.4	-	84.7	54.5

An *in-situ* 4-point resistance measurement as a function of temperature was performed at SUNY on two control samples in a vacuum chamber (with pressure ~10^{-6} torr) without oxygen under identical conditions as in CONCAP-II experiment. This procedure showed that the Y-Ba-Cu-O films degraded very badly which proves that the oxygen is needed to replenish the lost lattice oxygen in these films.

Notes on LANL-prepared HTSC thin films

LANL supplied 11 HTSC thin film samples out of which only four were R-measured (2 each on the ambient and 320° C hot plates) and the rest were passive samples. Figure 11 shows a spectrum of R/R$_o$ vs MET on the hot plate. This sample behaved in similar fashion as GE 1 sample described above. The resistance of this sample increased by ~1.5 times that of ambient values. There is not much change in slope and this film is unchanged during and after the flight. T_c remained the same. The second sample on the hot plate (figure 12) behaved differently. The resistance decreased by ~1.2 times the ambient value. A casual inspection of the curve shows that the resistance has gradually decreased with MET and reaches a value below that of ambient. This suggests that the sample has improved, but contact annealing is not ruled out. However, T_c dropped from 79 K to 36 K after the flight, which we are unable to explain.

CONCLUSIONS

Thin film HTSC devices of state-of-the-art quality were exposed unprotected to the low Earth orbital environment while being actively monitored. These materials have major potential for revolutionizing the communication and electronics industries in the 21st century, and a major satellite program is currently underway to demonstrate device operation at superconducting temperatures on orbit (the HTSSE program [10] of the Naval Research Laboratory). On the first flight of CONCAP-II, we have demonstrated the survivability of these materials exposed unprotected at ambient.

The resistance of the thin films was measured in flight during the oxygen exposure and heating cycle using a 4-point resistance measurement. Superconducting properties were measured in the laboratory before and after the flight by the individual experimenters. Films with good superconducting properties, and which were exposed to the oxygen atom flux, survived the flight, including those heated to 320° C (600 K) with properties essentially unchanged, while other samples that were heated, but not exposed to oxygen, were degraded. The properties of other flight controls held at ambient temperature appear unchanged and indistinguishable from those of ground controls, whether exposed to oxygen or not. The main objectives have been realized on STS-46 and due to experimental constraints, we could not determine if lost lattice oxygen may be replaced at relatively low temperatures by the fast O atom beam, which we seek to test in a re-flight of CONCAP-II in 1994.

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LEGEND

1) Controller
2) Battery
3) DC/DC Converter
4) Heater Switch
5) Fuse Box
6) Vertical Mounting Plate
7) Suspension Plate
8) GAS Mounting Plate
12) Experiment Insert Plate
13) Hot Plate
14) Sample Mask & Holders
15) Reflectometers
16) Cable Cut-out
17) Primary Bumpers
18) Secondary Bumpers
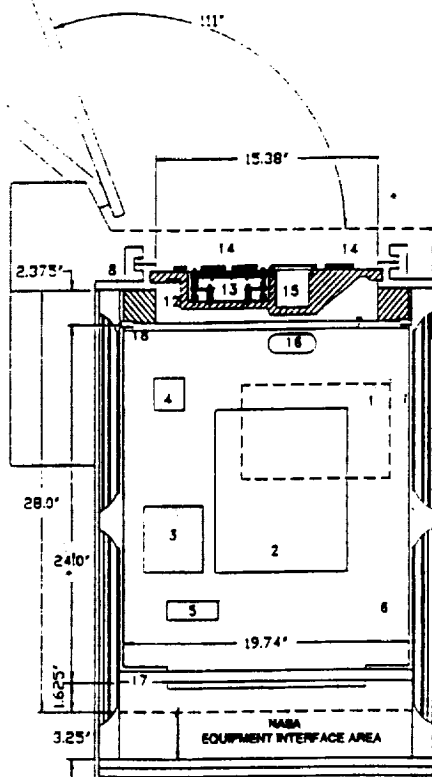
FIGURE 1:   CONCAP-II.01 Experiment Accommodation.
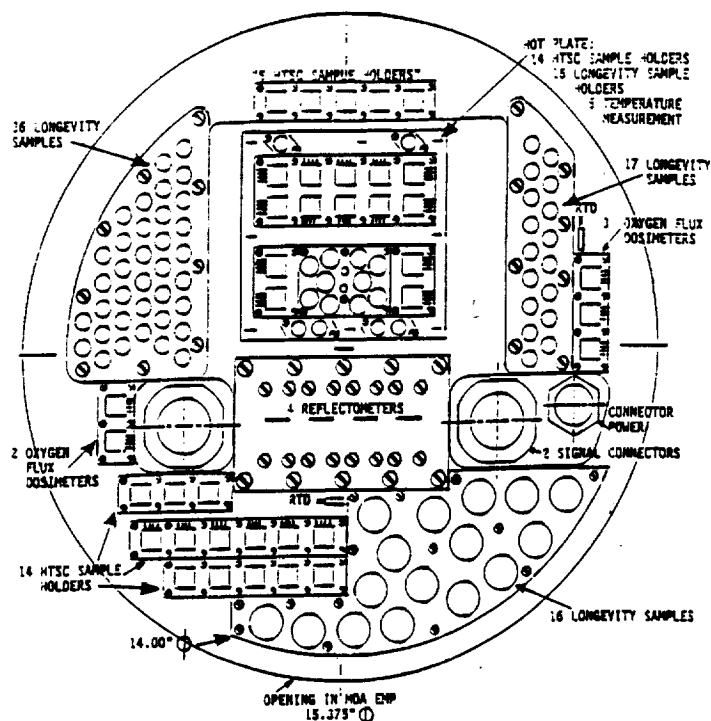
FIGURE 2:   Accommodation of sample holders on Experiment Insert Plate.

Top View

FLATPACK PN AFP -2001 - 001
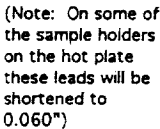
(Original leads: 0.500")
(Depth inside: 0.115")

Figure 3: A Sketch of the "FLATPACK" Sample Holder

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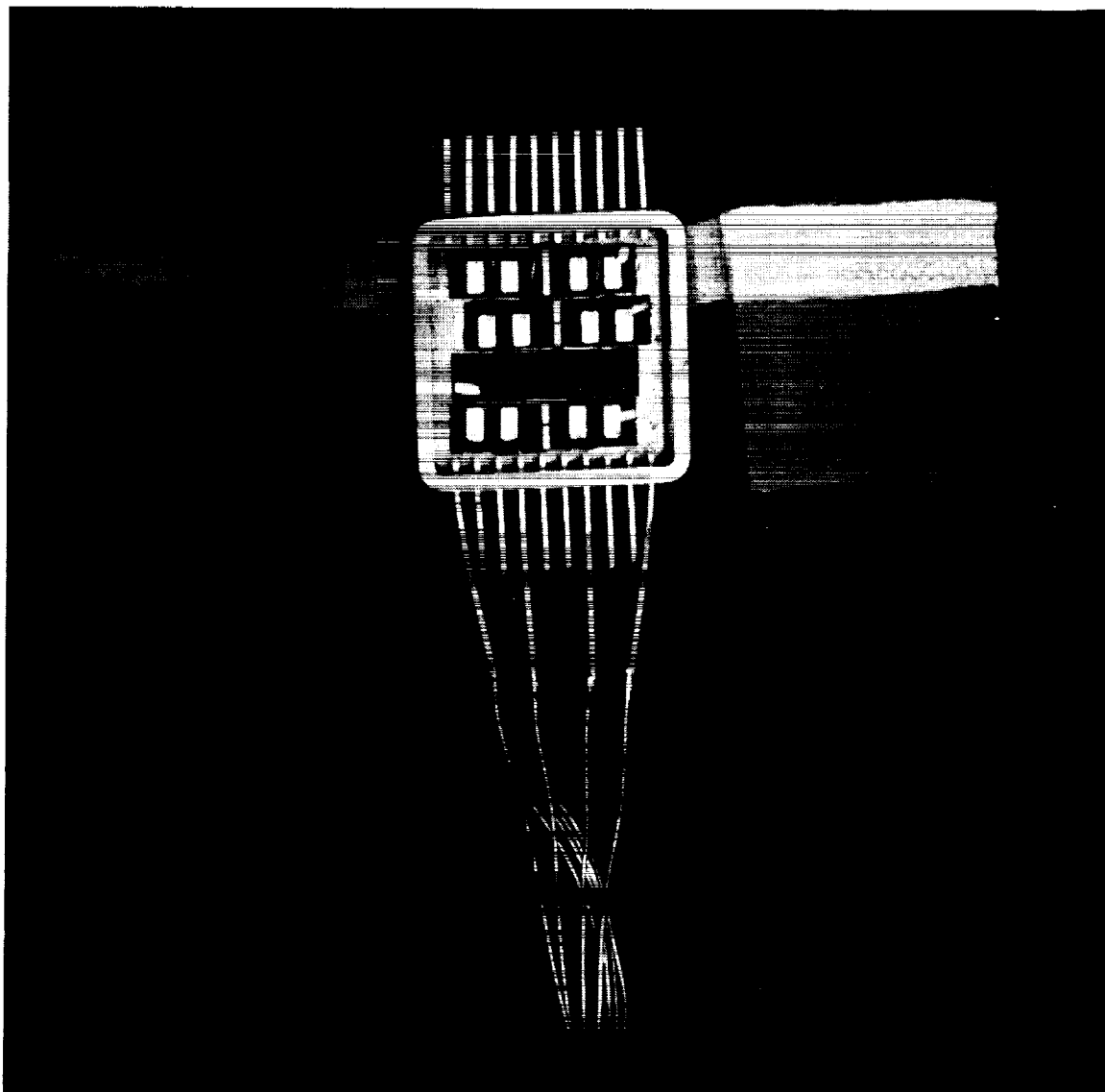
FIGURE 4: A photograph of the General Electric HTSC device mounted in a FLATPAX.
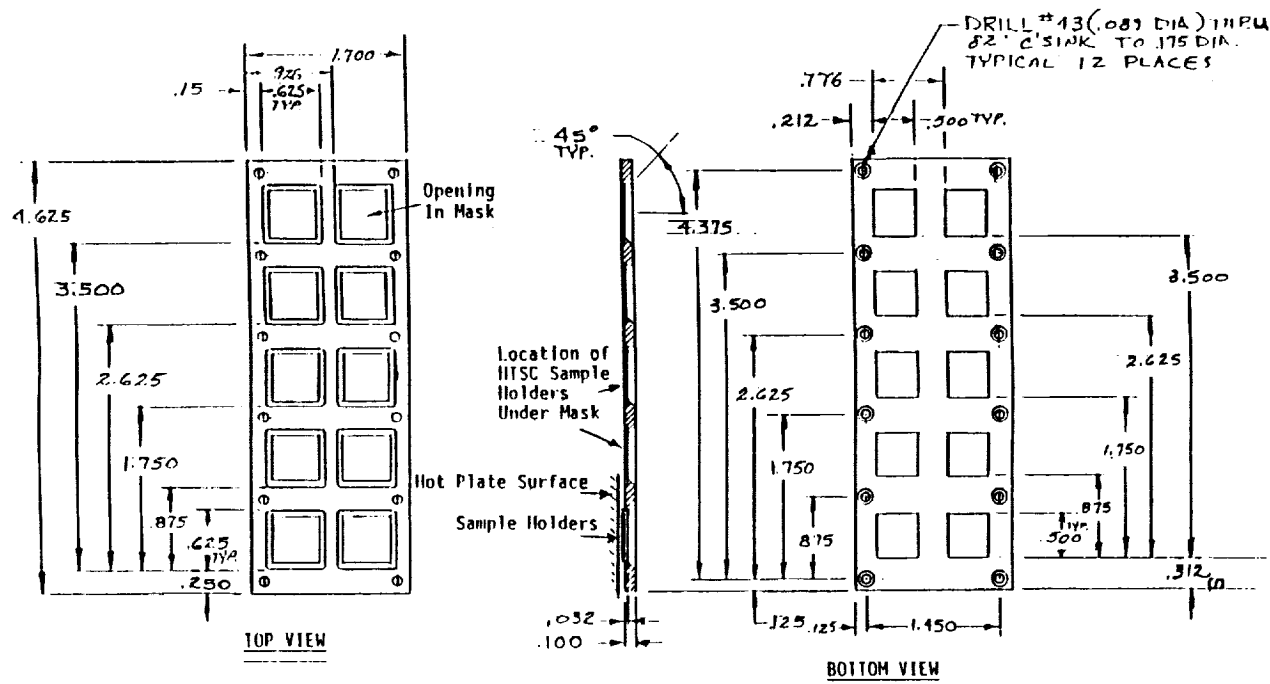
FIGURE 5: Mask for HTSC sample holders on the hot plate.
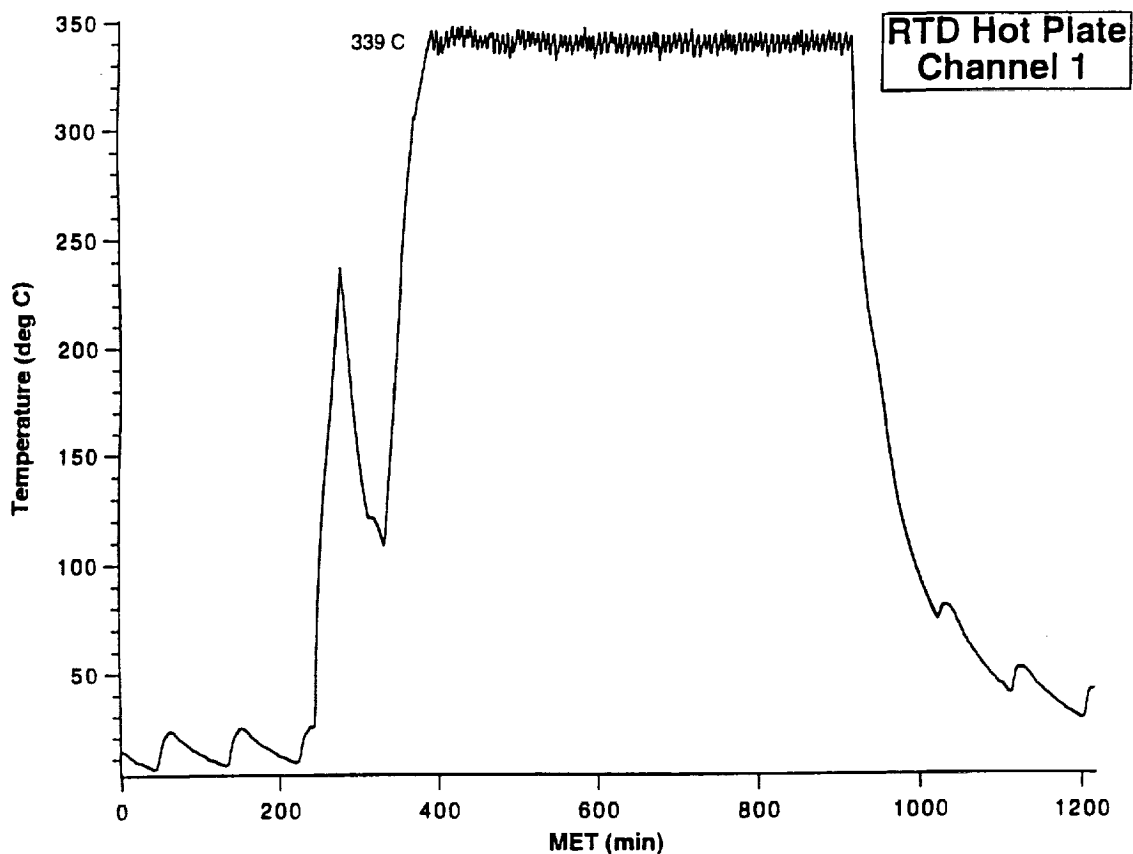
FIGURE 6: Temperature profile of the RTD on the 320°C hot plate during the 20 hr CONCAP-II.01 experiment.
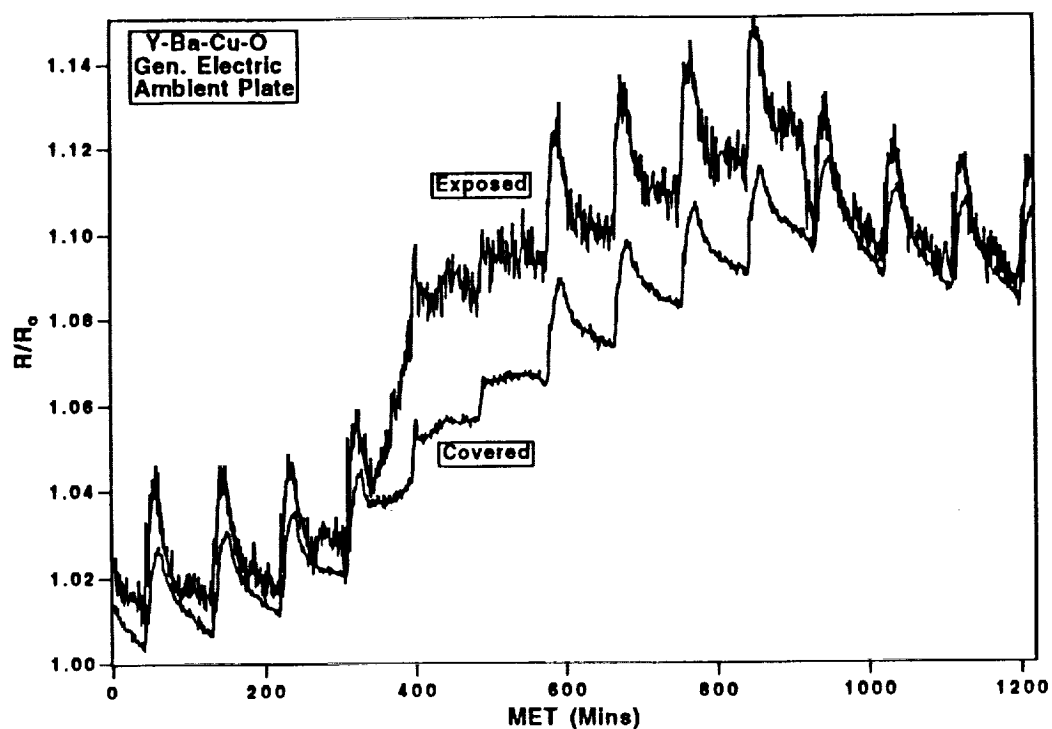
FIGURE 7: Mission Elapsed Time (Mins) versus normalized resistance of the General Electric HTSC sample #3 (Exposed) and #4 (covered) on the ambient plate.
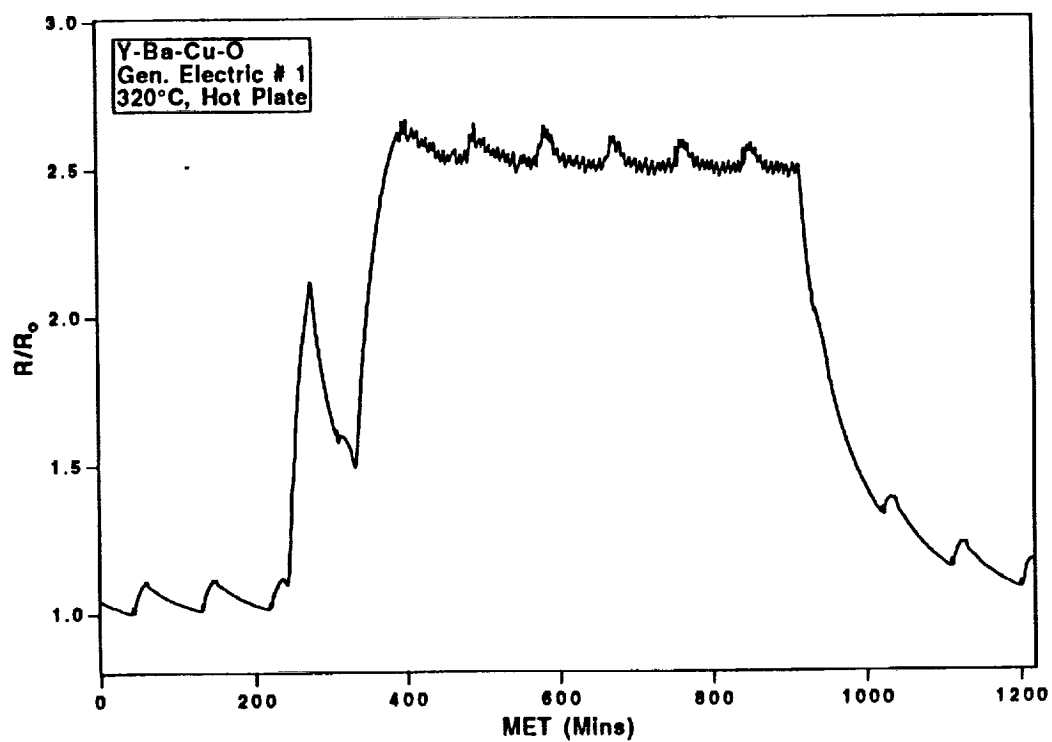
FIGURE 8 : Mission Elapsed Time (Mins) versus normalized resistance of the General Electric HTSC sample (#1) on the 320°C hot plate.
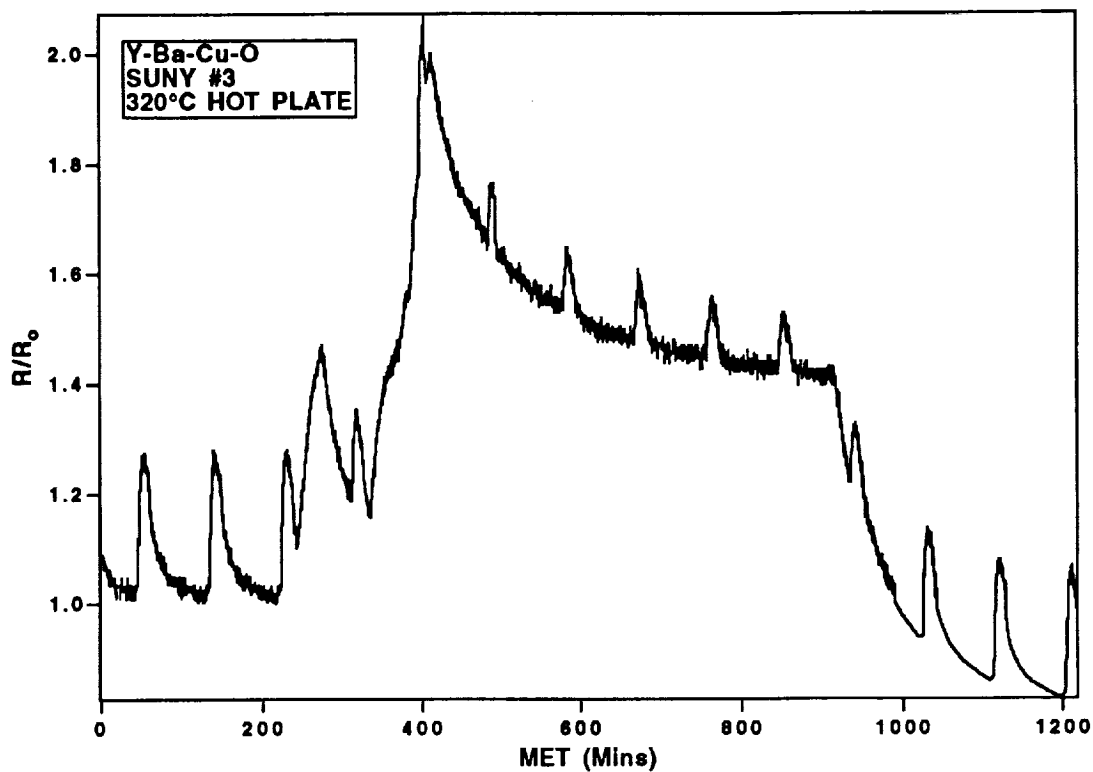
FIGURE 9: Mission Elapsed Time (Mins) versus normalized resistance
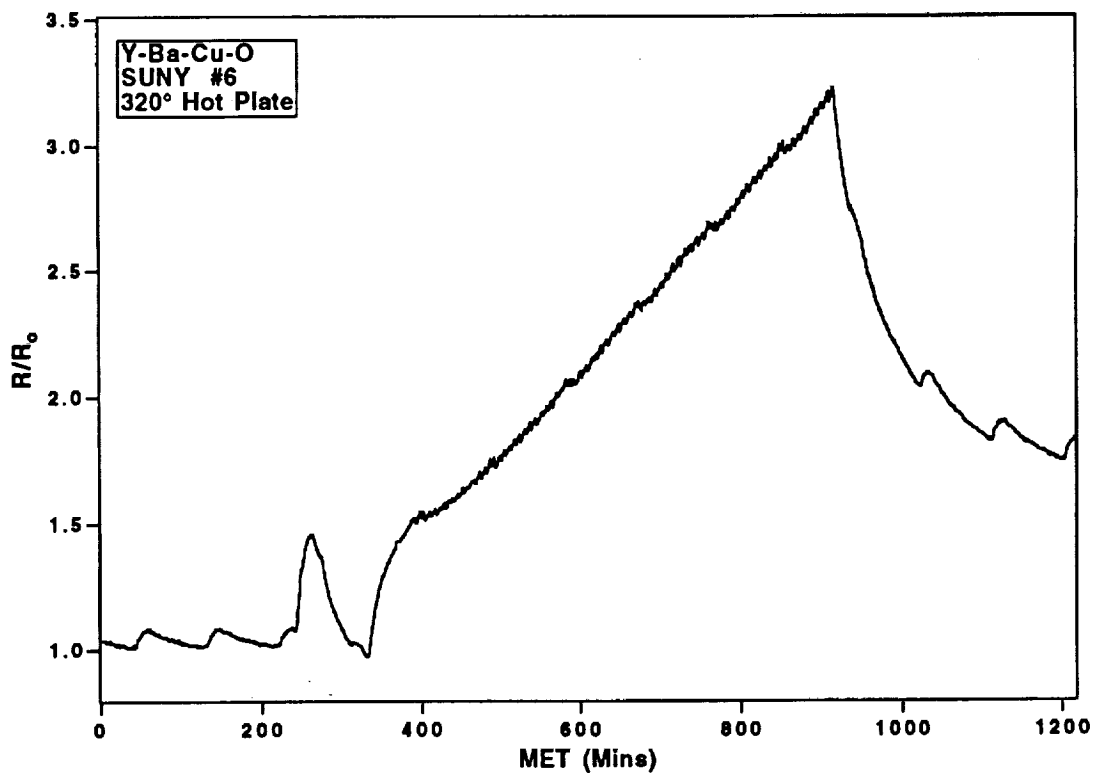of the SUNY HTSC sample (SUNY #3) on the 320°C hot plate.

FIGURE 10: Mission Elapsed Time (Mins) versus normalized resistance
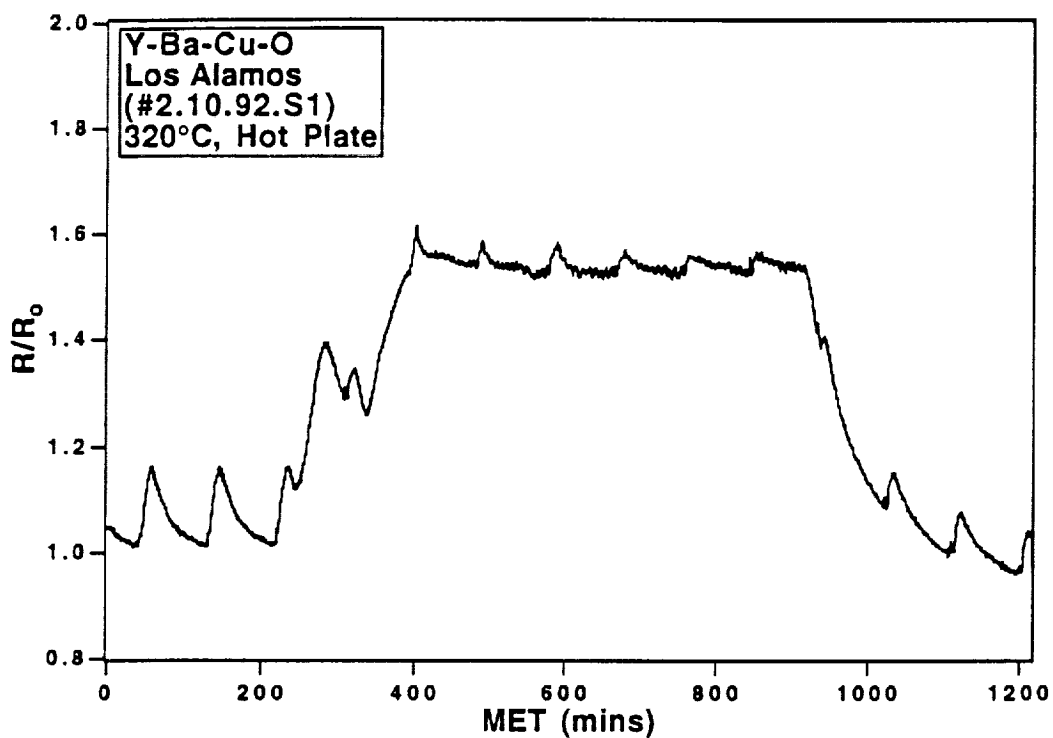of the SUNY HTSC sample (SUNY #6) on the 320°C hot plate.

FIGURE 11 : Mission Elapsed Time (Mins) versus normalized resistance
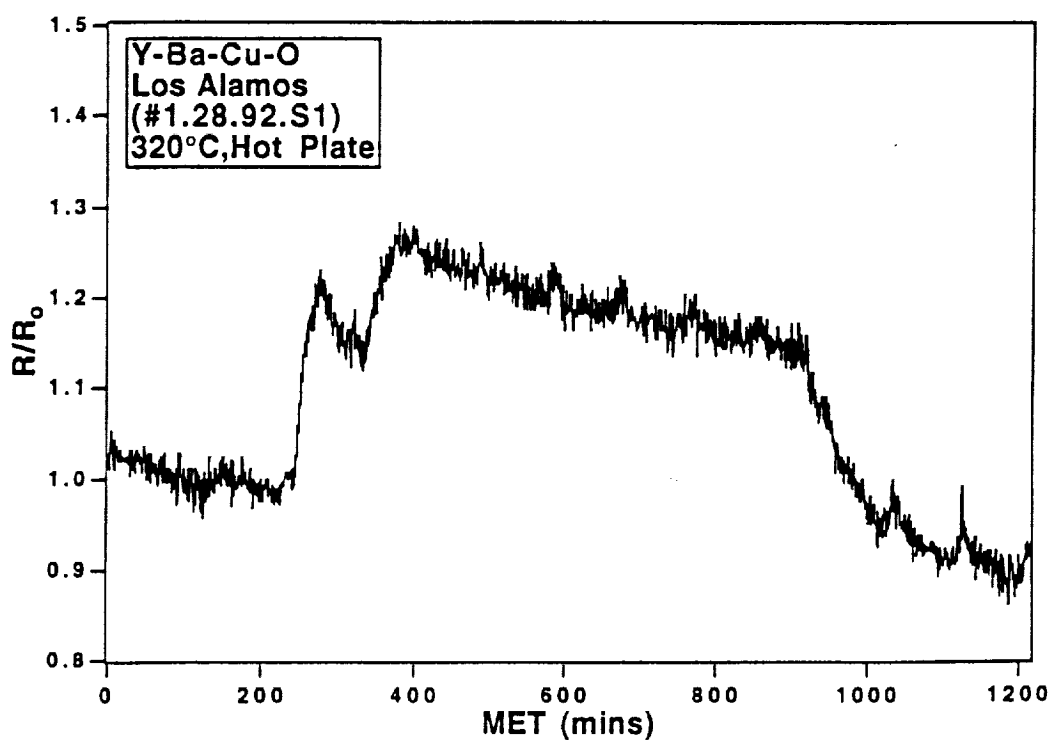of the Los Alamos HTSC sample (#2.10.92.S1) on the 320°C hot plate.

FIGURE 12 : Mission Elapsed Time (Mins) versus normalized resistance
of the Los Alamos HTSC sample (#1.28.92.S1) on the 320°C hot plate.